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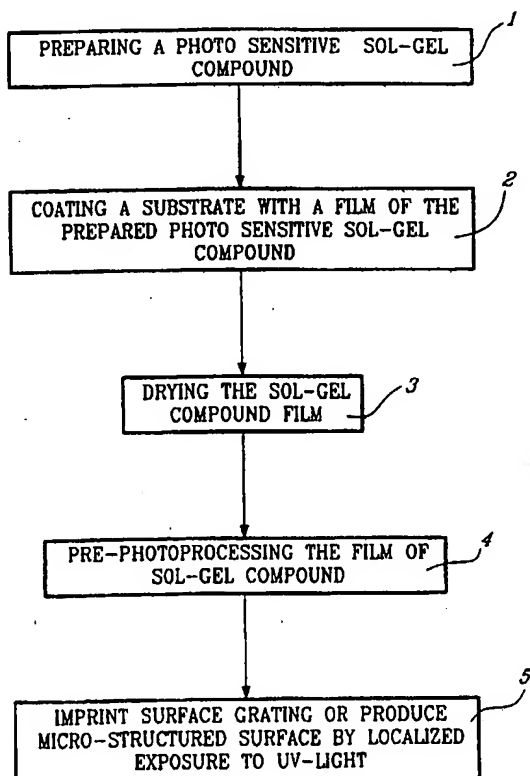
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(54) Title: SELF-PROCESSING OF DIFFRACTIVE OPTICAL COMPONENTS IN HYBRID SOL-GEL GLASSES



(57) Abstract: A simple process for producing controlled surface deformation in photosensitive hybrid sol-gel glass compounds is described with applications in the low-cost mass-production of micro-optical elements. Diffractive optical components are produced by first pre-photoprocessing a film of hybrid sol-gel glass compound to modify compressive and tensile stresses at the surface of the film and, then, exposing the pre-photoprocessed film to UV light through a mask to cause local densification and shrinkage of the illuminated areas. The present process does not involve any etching step and the diffractive components are resistant to temperature and solvent effects. Commercial applications are in the field of telecommunications, data communications and sensing, and more generally micro-structuration of surfaces.

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SELF-PROCESSING OF DIFFRACTIVE OPTICAL COMPONENTS IN HYBRID SOL-GEL GLASSES

BACKGROUND OF THE INVENTION

1. Field of the invention:

The present invention is concerned with a process for micro-structuring a surface and fabricating diffractive optical elements in self-processing photo-curable materials, without development following the exposure.

2. Brief description of the prior art:

The increased sophistication of high volume microfabrication and replication technologies has given fresh impetus to the use of miniature gratings as key components for applications in data communication, telecommunication and sensor devices. At this stage, manufacturing cost is of concern, which explains the growing interest in direct writing technologies that use light as the agent to create surface relief and/or index modification. Photoinduced surface deformation has been observed in a variety of photo-curable materials.

In dry photopolymer films for instance, monomer mass transport is responsible for relief formation [L. Lavielle, C. Croutx-Barghorn, E. Schuller, and D.J. Loughnot, "Self-organization in dry photopolymerized acrylate films. 2: General experimental description", J. Photochem. and Photobio. A **104**, pp. 213-216 (1997)]. When illuminated, these materials swell by monomer diffusion to create ridges in the regions exposed to light. Monomer diffusion tends to degrade the resolution and sub-micron feature sizes are difficult to imprint in these materials [[Hunsinger, J. J.; Simonin, L.; Gonnet, J. P.; Cros, B.; Loughnot, D. J., *Pure Appl. Opt.* **1995**, *4*, 529] [Krongrauz, V. V.; Legere-Krongrauz, C. C., *Polymer*, **1993**, *34*, 3614]]. Furthermore, photopolymers usually need a fixing step or a development step. More recently, surface gratings have been induced with visible light in azobenzene-containing polymer [[P. Rochon, E. Batalla, and A. Natansohn, "Optically induced surface gratings on azoaromatic polymer films", *Appl. Phys. Lett.* **66**, pp. 136-138 (1995)] [D.Y. Kim, S.K. Tripathy, Lian Li, and J. Kumar, "Laser-induced holographic surface relief gratings on nonlinear optical polymer films", *Appl. Phys. Lett.* **66**, pp. 1166-1168 (1995))] and sol-gel thin films [B. Darracq, F. Chaput, K. Lahlil, Y. Levy, and J.P. Boilot, "Photoinscription of surface relief gratings on Azo-Hybrid gels", *Advanced Materials* **10**, pp. 1133-1136 (1998)]. In these materials, the pattern is recorded with an interferometric technique where *trans-cis-trans* isomerization of the light-absorbing azo-groups causes spatially localized flow and compaction of the condensed phase host. In this class of material, the surface corrugation is erased when the material is heated to around 100°C. However, with few exceptions [[P. Rochon, E. Batalla, and A. Natansohn, "Optically induced surface gratings on azoaromatic polymer films", *Appl. Phys. Lett.* **66**, pp. 136-138 (1995)] [D.Y. Kim, S.K. Tripathy, Lian Li, and

J. Kumar, "Laser-induced holographic surface relief gratings on nonlinear optical polymer films", *Appl. Phys. Lett.* **66**, pp. 1166-1168 (1995)][B. Darracq, F. Chaput, K. Lahlil, Y. Levy, and J.P. Boilot, "Photoinscription of surface relief gratings on Azo-Hybrid gels", *Advanced Materials* **10**, pp. 1133-1136 (1998)] [T. Suzuki, Y. Todokoro, K. Komenou, "Process for the production of optical elements" U.S. Patent 4,877,717 (Oct. 1989)], surface corrugation has not been considered as a desirable effect and has not been used for device applications. Much effort has even been put into suppressing surface relief in hologram inscription or photoresist applications [P. Karrer, S. Corbel, J.C. Andre, and D.J. Loughnot, "Shrinkage effects in photopolymerizable resins containing filling agents: Application to stereophotolithography", *J. Poly. Sc. A: Poly. Chem.* **30**, pp. 2715-2723 (1992)].

The sol-gel glass process is highly versatile for fabricating photonic devices. Moreover, the introduction of organic components in the inorganic network permits further tailoring of chemical and physical properties of the glasses (improved mechanical properties, lower densification temperature, tailored refractive index, etc.). Photosensitivity has been demonstrated in acrylate-rich hybrid glasses where light initiates a chemical process that records the incident light pattern as a variation of polymerized and non-polymerized regions. Waveguides and diffractive elements have already been produced in acrylate-rich silica-zirconia compounds with a wet chemical etching step following the irradiation procedure [[H. Krug, and H. Schmidt, "Organic-inorganic nanocomposites for micro optical applications", *New J. Chem.* **18**, pp. 1125-1134 (1994)][S.I. Najafi, T. Touam, R. Sara, M.P. Andrews, and M.A. Fardad, "Sol-gel glass waveguide and grating on silicon", *J. Light.*

Techn. 16, pp. 1640-1646 (1998)][J.T. Rantala, P. Ayras, R. Levys, S. Honkanen, M.R. Descour and N. Peyghambarian, "Optical devices - Binary-phase zone-plate arrays based on hybrid solgel glass", Opt. Lett. 23, pp. 1939-1941 (1998)][P. Ayras, J. T. Rantala, S. Honkanen, S. B. Mendes, N. Peyghambarian, "Diffraction gratings in sol-gel films by direct contact printing using a UV-mercury lamp", Optics Communications 162, 215-218 (1999)]. The inventors have discovered that light-induced relief patterning can be performed in the same class of materials without requiring a subsequent etching process.

OBJECT OF THE INVENTION

An object of the present invention is therefore to provide a simple process for producing controlled surface deformation in sol-gel compounds with applications in the low-cost mass-production of micro-optical elements.

SUMMARY OF THE INVENTION

More specifically, in accordance with the present invention, there is provided a process of fabricating a diffractive optical component, comprising coating a substrate with a film of photosensitive sol-gel compound, pre-photoprocessing the film of photosensitive sol-gel compound, and imprinting a surface grating on the pre-photoprocessed

film of photosensitive sol-gel compound. Pre-photoprocessing the film of photosensitive sol-gel compound comprises flooding the entire surface of the film of photosensitive sol-gel compound with light, and modifying compressive and tensile stresses at the surface of the film of photosensitive sol-gel compound in response to the flooding light. Finally, Imprinting a surface grating on the pre-photoprocessed film of photosensitive sol-gel compound comprises locally exposing the pre-photoprocessed film of photosensitive sol-gel compound to light, and locally densifying and shrinking the pre-photoprocessed film of photosensitive sol-gel compound in response to that local light exposure.

In accordance with preferred embodiments of the diffractive optical component fabricating process:

- 15 - the photosensitive sol-gel compound is a hybrid sol-gel glass compound, the hybrid sol-gel glass compound is an acrylate-rich hybrid sol-gel glass compound, the acrylate-rich hybrid sol-gel glass compound is selected from the group consisting of: an acrylate-rich silica-titania compound; and an acrylate-rich silica-zirconia compound;
- 20 - the photosensitive hybrid sol-gel glass compound is doped with at least one metallic element selected from the group consisting of: titanium, vanadium, chromium, niobium, tantalum, tungsten, molybdenum, and zirconium;
- 25 - the substrate is selected from the group consisting of: glass substrates; paper substrates; metal substrates; plastic substrates; wood substrates;

dielectric substrates; and semiconductor substrates including silicon wafer substrates;

5 - the photosensitive sol-gel compound is an acrylate-rich silica-titania compound, and wherein the process comprises, prior to coating the substrate, preparing the photosensitive sol-gel compound by:

- preparing a hybrid organosilicate glass from methacryloxypropyl-trimethoxysilane, titanium (IV) isopropoxide, and methacrylic acid, wherein preparing a hybrid organosilicate glass comprises:

10 - conducting partial hydrolysis and polycondensation of the methacryloxypropyl-trimethoxysilane;

dissolving the titanium (IV) isopropoxide in isopropanol and complexing said titanium (IV) isopropoxide with methacrylic acid before dispersing said titanium (IV) isopropoxide into the silicon oxide system;

15 resuming hydrolysis and condensation of remaining silicon alkoxide functionalities and titanium propoxide;

adding a photoinitiator to the solution; and

filtering and aging said solution;

20 - preparing a hybrid organosilicate glass comprises introducing methacryloxypropyltrimethoxysilane, titanium (IV) isopropoxide, and methacrylic acid in a molar ratio of 10:2.5:2.5;

25 - conducting partial hydrolysis and polycondensation of the methacryloxypropyltrimethoxysilane comprises initiating said partial hydrolysis and polycondensation with 0.75 equivalent of acidified water;

- the acidified water is a 0.01M HCl acidified water.

- resuming hydrolysis and condensation of remaining silicon alkoxide functionalities and titanium propoxide comprises resuming the hydrolysis and condensation of the remaining silicon alkoxide functionalities and the titanium propoxide with the remaining equivalent of water, wherein total $H_2O:Si$ and $H_2O:Ti$ molar ratios are equal to 1.5;

- adding a photoinitiator to the solution comprises adding 3 wt % of Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide;

- aging the solution comprises allowing the solution to age for 24 hours;

- coating the substrate comprises spin-coating the substrate with the photosensitive sol-gel compound;

- the diffractive optical component fabricating process further comprises, prior to pre-photoprocessing the film of photosensitive sol-gel compound, drying this film by applying thereto a low power density UV-curing;

- flooding the entire surface of the film of photosensitive sol-gel compound with light comprises exposing the entire surface of the film of photosensitive sol-gel compound to light having a wavelength located in the range 200-450 nm, preferably 240-400 nm, during a time period located in a range extending from 10 seconds to 10 minutes, and with light having a power density of 10 mW/cm²;

- locally exposing the pre-photoprocessed film of photosensitive sol-gel compound to light comprises exposing the pre-photoprocessed film of photosensitive sol-gel compound to UV-light, either through an amplitude mask in a contact transfer mode or a laser light beam through a phase mask in a proximity mode; and

- imprinting a surface grating comprises controlling a peak-to-valley depth of the surface grating in relation to a degree of modification of the compressive and tensile stresses at the surface of the film of the photosensitive sol-gel compound during the film pre-photoprocessing.

The above described process can be used, in general to micro-structure a surface, more specifically, producing a micro-structured surface on a film of photosensitive sol-gel compound.

An advantage of the process according to the invention is that it involves no etching or other type of development method. Also, the obtained diffractive optical components are resistant to changes in amplitude or period caused by changes in temperature or contact with solvents, like alcohols, ketones or water.

Commercial applications are, in particular but not exclusively, in the field of telecommunications, data communications and sensing.

The objects, advantages and other features of the present invention will become more apparent upon reading of the following non restrictive description of preferred embodiments thereof,

given by way of example only with reference to the accompanying drawings.

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BRIEF DESCRIPTION OF THE DRAWINGS

In the appended drawings:

10

Figure 1 is a flow chart showing the different steps of a preferred embodiment of the process according to the invention;

Figure 2 is a flow chart showing the different substeps involved in a pre-photoprocessing step of the process of Figure 1;

15

Figure 3 is an AFM (Atomic Force Microscope) three-dimensional view of a 4 μm -period grating UV-imprinted in a silica-titania sol-gel layer, where an amplitude chromium mask and a mercury lamp were used for imprinting;

20

Figure 4 is a photograph of the Fraunhofer diffraction pattern from a 4 μm -period grating imprinted in a silica-titania sol-gel layer;

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Figure 5 is an AFM three dimensional view of a 0.56 μm -period grating imprinted in a silica-titania sol-gel layer, where a phase mask in proximity mode and an ArF excimer laser were used for imprinting;

Figure 6 is an AFM three-dimensional view of two 4 μm -period gratings recorded orthogonally to each other in a silica-zirconia sol-gel layer;

5

Figure 7 is a photograph of the Fraunhofer diffraction pattern from two 4 μm -period gratings recorded orthogonally to each other in a silica-zirconia sol-gel layer;

10

Figure 8 is an AFM three dimensional view showing the absence of swelling at the edge of the grating when sample was UV-cured with a mercury lamp (3 mW/cm^2 for 5 min) before imprinting;

15

Figure 9 is an AFM three dimensional view illustrating the swelling occurring at the edge of a grating recorded in a silica-zirconia sol-gel layer, where the sample was prebaked in an oven at 110°C for 30 min. before imprinting; and

20

Figures 10a and 10b are cross-sectional views showing the mechanism of formation of surface corrugation in an acrylate-rich hybrid sol-gel according to the present invention, where Figure 10a shows a cross-section of the sample before UV-irradiation and Figure 10b shows a cross-section of the sample after UV-irradiation.

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DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Although the preferred embodiment of the present invention
5 relates to a process for fabricating diffractive optical components, it
should be kept in mind that the present invention is not confined to that
particular application as will be described hereinafter.

10 The process according to this preferred embodiment, for
fabricating diffractive optical components comprises the following steps:

- (a) preparing a photosensitive sol-gel compound (step 1 of Figure
1) :

15 As an example, the synthesis of a photosensitive hybrid sol-gel
glass compound, namely acrylate-rich silica-titania compound, will be
described.

20 For obtaining acrylate-rich silica-titania compound, a hybrid
organosilicate glass is prepared from methacryloxypropyl-
trimethoxysilane, titanium (IV) isopropoxide, and methacrylic acid. As an
example, methacryloxypropyltrimethoxysilane, titanium (IV) isopropoxide,
and methacrylic acid are included in a molar ratio of 10:2.5:2.5. Partial
hydrolysis and polycondensation of methacryloxypropyltrimethoxysilane
25 was initiated with 0.75 equivalent of acidified water, for example a 0.01M
HCl acidified water. In a second step, titanium (IV) isopropoxide was
dissolved in isopropanol and complexed with methacrylic acid before
being dispersed into the resulting silicon oxide network. Hydrolysis and

condensation of the remaining silicon alkoxide functionalities and the titanium propoxide were resumed with the remaining equivalent of water, wherein total $H_2O:Si$ and $H_2O:Ti$ molar ratios are equal to 1.5. In order to initiate photopolymerization in further processing steps, a photoinitiator (3 wt % of Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide, Irgacure 819, CIBA Geigy) was added to the resulting solution which was filtered and allowed to age for 24 hours before use.

Of course, this is within the scope of the present invention to implement the present invention using other photosensitive hybrid sol-gel glass compounds such as any polymerizable organometallic starting compounds, including acrylate-, vinyl-, epoxy-based compounds.

The hybrid glass may be doped with metallic elements other than titanium. Hybrid glass can be provided without metallic doping or combined with metallic elements in the form of alkoxides or halides (usually chlorides) of vanadium, chromium, niobium, tantalum, tungsten, molybdenum, zirconium, and thus preferably with metal elements drawn from the early portion of the periodic table. The metal can also be added in the form of minute particles of the metal oxide, including for example but not exclusively aluminium oxide, whose diameter is smaller than the wavelength of light in order to avoid opacity and optical scattering.

The purpose of adding the metals can be to raise the refractive index of the hybrid glass above the refractive index of the hybrid glass without metal. The reason for this is to allow the Bragg grating to be included as part of an optical waveguide; it may be desired to have the

waveguide created with a refractive index higher than the refractive index of its surrounding media in order to guide light.

Most significantly, the metal is added to modify the structural properties of the glass, including hardness, which is particularly relevant to making Bragg gratings that show increased stability to resist changes in the dimensions of the grating due to the effects of heating or cooling or exposure to solvents.

Similar components have been fabricated using the process according to the preferred embodiment with acrylate-rich silica-zirconia compounds. However, the process of surface relief formation was found to be more effective and the components more temperature resistant when titania was incorporated into the silica network.

(b) coating (step 2 of Figure 1) of a glass or silicon wafer substrate with the photosensitive hybrid sol-gel glass compound (typical film thickness obtained by spin-coating at 5000 rpm for 60 sec was around 5 μm):

The substrate can also be made of other materials such as paper, metal, plastic, wood, most dielectrics, and semiconductors. Also, processes other than spin-coating can be used to coat the substrate with photosensitive sol-gel compound.

(c) drying the film of sol-gel compound (step 3 of Figure 1) with a low power density UV-curing;

As a non limitative example, a UV low power density of 3 mW/cm² from a mercury lamp was applied for 5 minutes to at least partially dry the coated substrate. Other processs such as oven-drying and exposure to visible light, infrared radiation or microwave radiation could also be used for drying the sol-gel compound.

(d) pre-photoprocessing the film of photosensitive hybrid sol-gel glass compound (step 4 of Figure 1):

To ensure that the diffractive optical component is of the self-processing kind, the surface of the film of photosensitive hybrid sol-gel glass compound is subjected to a pre-photoprocessing step. The purpose of pre-photoprocessing the film of photosensitive hybrid sol-gel glass compound is to modify the compressive and tensile stresses in the film, in particular at the surface of the film, to add control over the peak-to-valley depth of the diffraction grating that is subsequently formed.

Also, the pre-photoprocessing step further dries the surface of the film to ensure that this film will not adhere to the photomask when this mask is contacted with the surface of the film during writing of the grating.

This pre-photoprocessing step comprises exposing, more specifically flooding the entire surface of the film of photosensitive hybrid sol-gel glass compound with light (step 21 of Figure 2). As a non limitative example, the power density of the flooding light will be of the order of 10 mW/cm². This light may be in the wavelength range 200-450 nm, preferably in the range 240-400 nm. This pre-photoprocessing step

is conducted over a range of time extending from 10 seconds to 10 minutes, depending on the intensity and wavelength of the light and the desired effect. A light-exposure time of 30 seconds is usually preferred. This pre-photoprocessing step may be conducted at or above room temperature.

Those of ordinary skill in the art will appreciate that pre-photoprocessing involves parameters such as the power density of the flooding light, the wavelength of the flooding light, the time of exposure of the film to the flooding light, and the temperature which can be selected to modify the compressive and tensile stresses in the film, in particular at the surface of the film (step 22 of Figure 2) as required to obtain the desired control over the peak-to-valley depth of the diffraction grating (step 23 of Figure 2) that is subsequently formed.

(e₁) exposing the sample to UV-light through an amplitude mask in a contact transfer mode.

(e₂) an alternative to step e₁ is to expose the sample to a UV laser light beam through a phase mask in a proximity mode.

Other available processes such as UV, visible or infrared laser beam interference (holography) can also be used to locally expose the sample and imprint the surface grating. Further available processes comprise, amongst others, exposure of the sample to a laser beam through a grey-scale mask, direct laser writing and other interferometric techniques.

Local exposure of the film of photosensitive hybrid sol-gel glass compound to UV light through a mask causes local densification and shrinkage of the illuminated area in order to imprint the desired surface grating of the diffractive optical component. As explained
5 hereinabove, it should be kept in mind that the pre-photoprocessing greatly influences the peak-to-valley depth of the grating.

The process according to this preferred embodiment is enabled by crosslinking occurring in the photosensitive hybrid sol-gel glass compound. The process of crosslinking to produce a networked
10 hybrid glass consist of two steps.

In the first step, the alkoxides, for example methacryloxypropyltrimethoxysilane are caused to undergo hydrolysis and polycondensation by acid catalysed decomposition of the silico-alkoxide bond. This polycondensation reaction generates a colloidal
15 suspension called a sol. The sol phase is spin- or dip-coated to make a film. The process of film formation is accompanied by further crosslinking reactions to make silicon-oxygen-silicon bonds throughout the film. In forming the film in this manner, the material enters a gel phase.
20

Since one bond to silicon contains an organic substituent (an olefin) that can be caused to polymerize when exposed to light, a second crosslinking step can be introduced. This occurs when the olefin
25 polymerizes with other olefin moieties in the film of the glass. In this manner, crosslinks involving silicon-carbon-silicon bonds are obtained in the matrix film. Thus the self-processing operation takes place when the

photosensitive hybrid sol-gel glass compound is exposed to light and the film responds by producing a polyolefin within the glass.

The following non limitative examples are given to illustrate but not limit, with respect to period and amplitude, the process of surface relief formation in photosensitive acrylate-rich sol-gel glass compounds such as acrylate-rich silica-titania compound and acrylate-rich silica-zirconia compound. In these three examples, prior to imprinting the gratings, a UV low power density of 3mW/cm^2 from an unfiltered mercury lamp was applied for 5 minutes to partially dry the covered substrate. Pre-photoprocessing of the film was subsequently conducted by flooding the entire surface of the film with light having a wavelength of 313 nm selected by a band-pass filter, and a power density of 10 mW/cm^2 for an exposure time of 5 minutes at room temperature. Then:

- diffraction gratings with periods ranging from 4 to $1.4\text{ }\mu\text{m}$ (Figures 3 and 4) were fabricated in $5\text{ }\mu\text{m}$ thick films by illuminating the sample through an amplitude chromium mask at quasi-normal incidence with non-collimated UV light from a mercury lamp (power density measured at 254 nm before the mask was 90 mW.cm^{-2});

- diffraction gratings with a period of $0.56\text{ }\mu\text{m}$ (Figure 5) were fabricated by illuminating the sample through a phase mask at quasi-normal incidence with an ArF excimer laser at 193 nm (20mJ per pulse, repetition rate 12 Hz and 120 seconds exposure time); and

- two 4 μm -period gratings were recorded at 90° from each other with a mercury lamp to demonstrate the possibility of multiple recording in the material (Figures 6 and 7);

5 General purpose and commercial applications:

10 The materials, fabrication processes and features of the diffractive optical components according to the present invention make them attractive in particular but not exclusively for telecommunication, data telecommunication and sensor applications including but not restricted to:

- wavelength-division multiplexers and filters;

15 - gratings for use in distributed-feedback and distributed-Bragg reflector laser configurations;

- waveguide couplers or more generally resonant devices;

20 - variable tunable diffraction gratings;

- free space wave grating-based optical sensors like displacement sensors;

25 - due to the stability of the material in presence of water or solvent, a whole range of bio-chemical sensors based on the association of a waveguide and a diffraction grating, or a surface and a diffraction grating;

- gratings in micro-spectrometers; and

- optical interconnection schemes, including but not restricted to planar lightwave circuit (optical chip)-to-planar lightwave circuit coupling, and inter layer coupling of light.

Applications of the present invention to fields other than fabrication of optical elements can also be contemplated, for example:

- security and authenticity products; and

- applications where micro-structuration of a surface is required to modify the flow of a fluid against this surface.

Advantages and improvements related to the fabrication process:

- no etching step: this self-processing process requires no etching or other development step, and is therefore a short technological process;

- no pre-baking step: drying of the coating of photosensitive hybrid sol-gel glass compound is done by the above drying and pre-photoprocessing steps. This contributes to a short processing time.

Furthermore it was discovered by the inventors named in the present patent application that low power UV light irradiation prior to grating inscription avoided swelling of the film on the edge of the component.

On the opposite, a noticeable swelling was observed when the

sample was oven-dried. Figures 8 and 9 show the effect of pre-UV and pre-bake on the edges of gratings recorded in silica-zirconia sol-gel films (the same effect was observed on silica-titania films);

5 - no fixing step : the corrugation is stable even in the absence of any photo or thermal post-treatment;

 - compatible with the use of masks which is cheaper than e-beam (electron beam) writing and more versatile than holographic exposure techniques;

10

 - sinusoidal profile due to the self-processing mechanism. This reduces the diffraction efficiency of higher harmonic orders;

15 - tunable amplitude of corrugation: the amplitude of the photo-induced surface corrugation was found to be dependent on the the conditions of UV dose and exposure time in both the pre-photoprocessing and grating writing steps. It varied also with the feature size of the pattern to be imprinted in the film. For a 4 μm -period grating, the amplitude of the corrugation obtained with an UV source (in the above described example, typically 90 $\text{mW}\cdot\text{cm}^{-2}$) could be as large as 800 nm. Amplitude of the 0.56 μm -period grating obtained with the excimer laser was around 110 nm;

20

25 - small values of surface roughness: thanks to the absence of etching step, the roughness of the corrugated surface is small. The root mean square value of the roughness R_q , measured by atomic force microscopy on a $100\times 100\text{ nm}^2$ area is smaller than 0.5

nm and can be as low as 0.1 nm, depending on the processing conditions;

Advantages and improvements related to the material:

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- smaller accessible feature sizes: the localized densification and shrinkage of the sol-gel material corresponds to the illuminated regions through the opening of the mask. The formation of photo-relief in this acrylate-containing hybrid sol-gel glass compound (Figure 10) differs from grating formation by diffusion of monomer in viscous thick film acrylates, or relief due to *trans-cis-trans* isomerization in media containing azo chromophores. Densification is caused by C-C bond formation during organic polymer chain growth, which induces collateral structural relaxation and condensation reactions in the metastable silica network [Saravanamuttu, K.; Du, W. M.; Najafi, S. I.; Andrews, M. P.; "Photoinduced Structural Relaxation and Densification in Sol-Gel Derived Nanocomposite Thin Film: Implications for Integrated Optics Device Fabrication"; *Can. J. Chem.*, **1998**, 76, pp.1717-1729]. In the hybrid sol-gel glass compounds, diffusion of monomer will be strongly suppressed because the acrylate moieties are either chelated to titania or covalently bound through silicon to the silica network. The polymerization is highly spatially confined, and in fact considerably more than what occurs in some photopolymers where monomer diffusion degrades resolution [K. Saravanamuttu, M. P. Andrews and S. I. Najafi, *Proc. SPIE Opt. Eng.* **3417**, (1998)]. Therefore, the 0.56- μ m-period grating which is given above as an example of application is by no means a limit in feature size;

- high transmittance of the material: the material is transparent in the visible-near infrared region and is therefore suitable for various applications within this spectral range. This is not the case of the azo-containing materials which absorb in the green region of the spectrum;

- versatility of the material: the material is compatible with most commonly used substrates, including silicon, glass and metals. The composition of the material can be tuned to vary the refractive index and other physical properties. The photoinitiator can also be changed according to the thickness of the section to be cured or the wavelength used; and

- robustness of the material: after UV inscription the components are solvent-resistant (water, acetone, isopropanol) and can be heated to temperature as high as 220°C for silica-titania compounds and 180°C for silica-zirconia compounds without any deterioration of the diffraction efficiency. This is not the case of azo-containing materials or of most photopolymers which do not stand so high temperatures. Also, no changes in the diffraction efficiency were measured when the gratings were submitted to post-UV exposure (10 mW/cm² for 30 min).

The following Table 1 shows typical experimental and theoretical values of diffraction efficiencies (η) transmitted in the various orders (wavelength is 0.6328 μm). All gratings were UV-imprinted according to the present invention in silica-titania sol-gel films. Gratings 1 and 2 were

5 imprinted with a mercury lamp through an amplitude chromium mask. Grating 3 was imprinted with an ArF excimer laser through a phase mask. The amplitude of the surface corrugation measured by atomic force microscopy is represented by "h". Discrepancies between theoretical and experimental values can be explained by the profile of the corrugated grating which is not perfectly sinusoidal.

	Experimental	Theoretical
Grating 1 : Λ (period) = 4 μm (h = 790 nm)	$\eta_0 = 3.3 \%$ $\eta_{\pm 1} = 34.6 \%$ $\eta_{\pm 2} = 11.6 \%$ $\eta_{\pm 3} = 2 \%$	$\eta_0 = 6.1 \%$ $\eta_{\pm 1} = 34.8 \%$ $\eta_{\pm 2} = 12.1 \%$ $\eta_{\pm 3} = 0.05 \%$
Grating 2 : $\Lambda = 1.4 \mu\text{m}$ (h = 230 nm)	$\eta_0 = 85.7 \%$ $\eta_{\pm 1} = 7.1 \%$	$\eta_0 = 82.3 \%$ $\eta_{\pm 1} = 8.8 \%$
Grating 3 : $\Lambda = 0.56 \mu\text{m}$ (h = 115 nm)	$\eta_0 = 96.5 \%$ $\eta_{\pm 1} = 3.5 \%$	$\eta_0 = 97.3 \%$ $\eta_{\pm 1} = 2.7 \%$

10 The present invention finds applications in the micro-structuration of surfaces both in the field of optics:

- to fabricate:

15 - diffractive optical components as described above, including a surface grating;

- Diffractive Optical Elements (DOE) comprising, but not restricted to, focussing elements such as lenses, including Fresnel lenses;

5

- refractive microlenses with large focal length and small aperture;

10

- ridge waveguides and waveguide gratings; and

- photonic band gap devices such as optical filters (not based on simple grating diffraction);

and out of the field of optics:

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- in the micro-structuration of surfaces to modify the flow at the air/solid, air/liquid or liquid/solid interfaces.

20

Although the present invention has been described hereinabove by way of a preferred embodiment thereof, this embodiment can be modified at will, within the scope of the appended claims, without departing from the spirit and nature of the subject invention.

WHAT IS CLAIMED IS:

1. A process of fabricating a diffractive optical component, comprising:

5 coating a substrate with a film of photosensitive sol-gel compound;
 pre-photoprocessing the film of photosensitive sol-gel compound, said
 film pre-photoprocessing comprising;

 flooding the entire surface of the film of photosensitive sol-
 gel compound with light; and

10 modifying compressive and tensile stresses at the surface
 of the film of photosensitive sol-gel compound in response to said
 flooding light; and

 imprinting a surface grating on the pre-photoprocessed film of
 photosensitive sol-gel compound, said surface grating imprinting
15 comprising:

 locally exposing the pre-photoprocessed film of
 photosensitive sol-gel compound to light; and

 locally densifying and shrinking the pre-photoprocessed
 film of photosensitive sol-gel compound in response to said local
20 light exposure.

2. A diffractive optical component fabricating process according
to claim 1, wherein the photosensitive sol-gel compound is a hybrid sol-
gel glass compound.

25

3. A diffractive optical component fabricating process according
to claim 2, wherein the hybrid sol-gel glass compound is an acrylate-rich
hybrid sol-gel glass compound.

4. A diffractive optical component fabricating process according to claim 3, wherein the acrylate-rich hybrid sol-gel glass compound is selected from the group consisting of: an acrylate-rich silica-titania compound; and an acrylate-rich silica-zirconia compound.

5. A diffractive optical component fabricating process according to claim 2, wherein the photosensitive hybrid sol-gel glass compound is doped with at least one metallic element selected from the group consisting of: titanium, vanadium, chromium, niobium, tantalum, tungsten, molybdenum, and zirconium.

6. A diffractive optical component fabricating process according to claim 1, wherein the substrate is selected from the group consisting of: glass substrates; paper substrates; metal substrates; plastic substrates; wood substrates; dielectric substrates; and semiconductor substrates including silicon wafer substrates.

7. A diffractive optical component fabricating process according to claim 1, wherein the photosensitive sol-gel compound is an acrylate-rich silica-titania compound, and wherein said process comprises, prior to coating the substrate, preparing the photosensitive sol-gel compound by:

preparing a hybrid organosilicate glass from methacryloxypropyl-trimethoxysilane, titanium (IV) isopropoxide, and methacrylic acid, wherein preparing a hybrid organosilicate glass comprises:

conducting partial hydrolysis and polycondensation of the methacryloxypropyl-trimethoxysilane;

dissolving the titanium (IV) isopropoxide in isopropanol and complexing said titanium (IV) isopropoxide with methacrylic acid before dispersing said titanium (IV) isopropoxide into the silicon oxide system;

resuming hydrolysis and condensation of remaining silicon alkoxide functionalities and titanium propoxide;

adding a photoinitiator to the solution; and

filtering and aging said solution.

8. A diffractive optical component fabricating process according to claim 7, wherein preparing a hybrid organosilicate glass comprises introducing methacryloxypropyl-trimethoxysilane, titanium (IV) isopropoxide, and methacrylic acid in a molar ratio of 10:2.5:2.5.

9. A diffractive optical component fabricating process according to claim 7, wherein conducting partial hydrolysis and polycondensation of the methacryloxypropyl-trimethoxysilane comprises initiating said partial hydrolysis and polycondensation with 0.75 equivalent of acidified water.

10. A diffractive optical component fabricating process according to claim 9, wherein the acidified water is a 0.01M HCl acidified water.

11. A diffractive optical component fabricating process according to claim 9, wherein resuming hydrolysis and condensation of remaining silicon alkoxide functionalities and titanium propoxide comprises

resuming the hydrolysis and condensation of the remaining silicon alkoxide functionalities and the titanium propoxide with the remaining equivalent of water, wherein total $H_2O:Si$ and $H_2O:Ti$ molar ratios are equal to 1.5.

5

12. A diffractive optical component fabricating process according to claim 7, wherein adding a photoinitiator to the solution comprises adding 3 wt % of Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide.

10

13. A diffractive optical component fabricating process according to claim 7, wherein aging the solution comprises allowing the solution to age for 24 hours.

15

14. A diffractive optical component fabricating process as recited in claim 1, wherein coating the substrate comprises spin-coating the substrate with the photosensitive sol-gel compound.

20

15. A diffractive optical component fabricating process as recited in claim 1, further comprising, prior to pre-photoprocessing the film of photosensitive sol-gel compound, drying said film of photosensitive sol-gel compound.

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16. A diffractive optical component fabricating process as recited in claim 15, wherein drying the film comprises applying to the film of photosensitive sol-gel compound a low power density UV-curing.

17. A diffractive optical component fabricating process as recited in claim 1, wherein flooding the entire surface of the film of photosensitive sol-gel compound with light comprises:

5 exposing the entire surface of the film of photosensitive sol-gel compound to light having a wavelength located in the range 200-450 nm.

18. A diffractive optical component fabricating process as recited in claim 17, wherein flooding the entire surface of the film of
10 photosensitive sol-gel compound with light comprises:

exposing the entire surface of the film of photosensitive sol-gel compound to light having a wavelength located in the range of 240-400 nm.

15 19. A diffractive optical component fabricating process as recited in claim 1, wherein flooding the entire surface of the film of photosensitive sol-gel compound with light comprises:

20 exposing the entire surface of the film of photosensitive sol-gel compound to light during a time period located in a range extending from 10 seconds to 10 minutes.

20. A diffractive optical component fabricating process as recited in claim 19, wherein flooding the entire surface of the film of photosensitive sol-gel compound with light comprises:

25 exposing the entire surface of the film of photosensitive sol-gel compound with light having a power density of 10 mW/cm².

21. A diffractive optical component fabricating process as recited in claim 1, wherein flooding the entire surface of the film of photosensitive sol-gel compound with light comprises:

5 exposing the entire surface of the film of photosensitive sol-gel compound with light:

having a wavelength located in the range of
240-400 nm;

having a power density of 10 mW/cm²; and

10 during a time period located between 10
second and 10 minutes.

22. A diffractive optical component fabricating process as recited in claim 1, wherein locally exposing the pre-photoprocessed film of photosensitive sol-gel compound to light comprises exposing the pre-
15 photoprocessed film of photosensitive sol-gel compound to UV-light.

23. A diffractive optical component fabricating process as recited in claim 1, wherein locally exposing the pre-photoprocessed film of photosensitive sol-gel compound to light comprises exposing the pre-
20 photoprocessed film of photosensitive sol-gel compound to UV-light through an amplitude mask in a contact transfer mode.

24. A diffractive optical component fabricating process as recited in claim 1, wherein locally exposing the pre-photoprocessed film of photosensitive sol-gel compound to light comprises exposing the pre-
25 photoprocessed film of photosensitive sol-gel compound to a UV laser light beam through a phase mask in a proximity mode.

25. A diffractive optical component fabricating process as recited in claim 1, wherein imprinting a surface grating comprises controlling a peak-to-valley depth of the surface grating in relation to a degree of modification of the compressive and tensile stresses at the surface of the film of the photosensitive sol-gel compound during the film pre-photoprocessing.

26. A process for micro-structuring a surface, comprising:
coating a substrate with a film of photosensitive sol-gel compound;
pre-photoprocessing the film of photosensitive sol-gel compound, said film pre-photoprocessing comprising;

flooding the entire surface of the film of photosensitive sol-gel compound with light; and

modifying compressive and tensile stresses at the surface of the film of photosensitive sol-gel compound in response to said flooding light; and

producing a micro-structured surface on the pre-photoprocessed film of photosensitive sol-gel compound, said micro-structured surface production comprising:

locally exposing the pre-photoprocessed film of photosensitive sol-gel compound to light; and

locally densifying and shrinking the pre-photoprocessed film of photosensitive sol-gel compound in response to said local light exposure.

27. A process for micro-structuring a surface according to claim 26, wherein:

the photosensitive sol-gel compound is a hybrid sol-gel glass compound;

the hybrid sol-gel glass compound is an acrylate-rich hybrid sol-gel glass compound; ;and

5 the acrylate-rich hybrid sol-gel glass compound is selected from the group consisting of:

an acrylate-rich silica-titania compound; and

an acrylate-rich silica-zirconia compound.

10 28. A process for micro-structuring a surface according to claim 26, wherein the photosensitive hybrid sol-gel glass compound is doped with at least one metallic element selected from the group consisting of: titanium, vanadium, chromium, niobium, tantalum, tungsten, molybdenum, and zirconium.

15 29. A process for micro-structuring a surface according to claim 26, wherein the substrate is selected from the group consisting of: glass substrates; paper substrates; metal substrates; plastic substrates; wood substrates; dielectric substrates; and semiconductor substrates including
20 silicon wafer substrates.

30. A process for micro-structuring a surface according to claim 26, wherein coating the substrate comprises spin-coating the substrate with the photosensitive sol-gel compound.

25 31. A process for micro-structuring a surface as recited in claim 26, further comprising, prior to pre-photoprocessing the film of

photosensitive sol-gel compound, drying said film of photosensitive sol-gel compound.

5 32. A process for micro-structuring a surface as recited in claim 31, wherein drying the film comprises applying to the film of photosensitive sol-gel compound a low power density UV-curing.

10 33. A process for micro-structuring a surface as recited in claim 26, wherein flooding the entire surface of the film of photosensitive sol-gel compound with light comprises:

 exposing the entire surface of the film of photosensitive sol-gel compound to light having a wavelength located in the range 200-450 nm.

15 34. A process for micro-structuring a surface as recited in claim 33, wherein flooding the entire surface of the film of photosensitive sol-gel compound with light comprises:

 exposing the entire surface of the film of photosensitive sol-gel compound to light having a wavelength located in the range of 240-400 nm.
20

 35. A process for micro-structuring a surface as recited in claim 26, wherein flooding the entire surface of the film of photosensitive sol-gel compound with light comprises:

25 exposing the entire surface of the film of photosensitive sol-gel compound to light during a time period located in a range extending from 10 seconds to 10 minutes.

36. A process for micro-structuring a surface as recited in claim 26, wherein flooding the entire surface of the film of photosensitive sol-gel compound with light comprises:

5 exposing the entire surface of the film of photosensitive sol-gel compound with light having a power density of 10 mW/cm².

37. A process for micro-structuring a surface as recited in claim 26, wherein flooding the entire surface of the film of photosensitive sol-gel compound with light comprises:

10 exposing the entire surface of the film of photosensitive sol-gel compound with light:

having a wavelength located in the range of
240-400 nm;

15 having a power density of 10 mW/cm²; and
during a time period located between 10
second and 10 minutes.

38. A process for micro-structuring a surface as recited in claim 26, wherein locally exposing the pre-photoprocessed film of
20 photosensitive sol-gel compound to light comprises exposing the pre-photoprocessed film of photosensitive sol-gel compound to UV-light.

39. A process for micro-structuring a surface as recited in claim 26, wherein locally exposing the pre-photoprocessed film of
25 photosensitive sol-gel compound to light comprises exposing the pre-photoprocessed film of photosensitive sol-gel compound to UV-light through an amplitude mask in a contact transfer mode.

40. A process for micro-structuring a surface as recited in claim 26, wherein locally exposing the pre-photoprocessed film of photosensitive sol-gel compound to light comprises exposing the pre-photoprocessed film of photosensitive sol-gel compound to a UV laser light beam through a phase mask in a proximity mode.

41. A process for micro-structuring a surface as recited in claim 26, wherein producing a micro-structured surface comprises controlling a peak-to-valley depth of the micro-structured surface in relation to a degree of modification of the compressive and tensile stresses at the surface of the film of the photosensitive sol-gel compound during the film pre-photoprocessing.

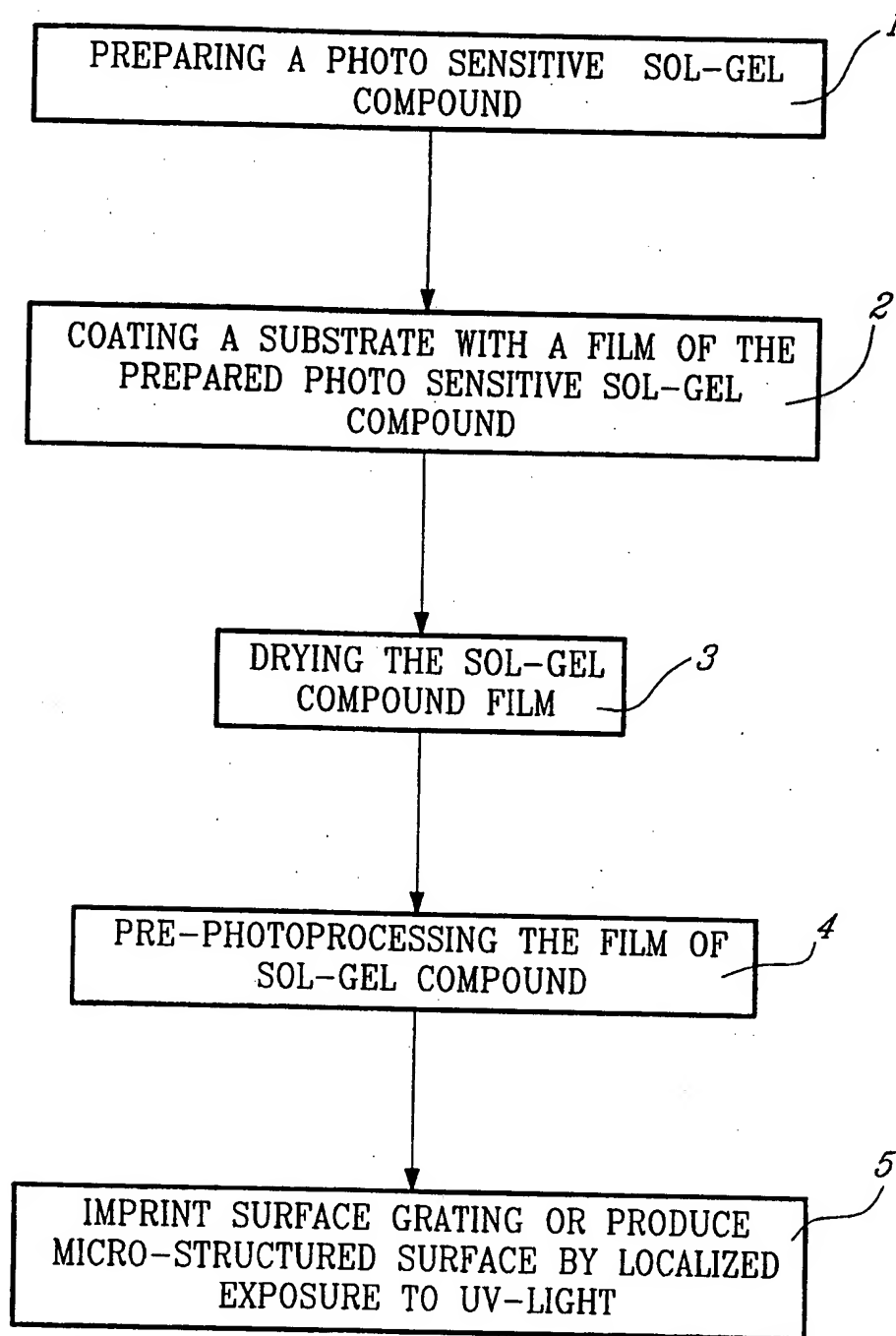
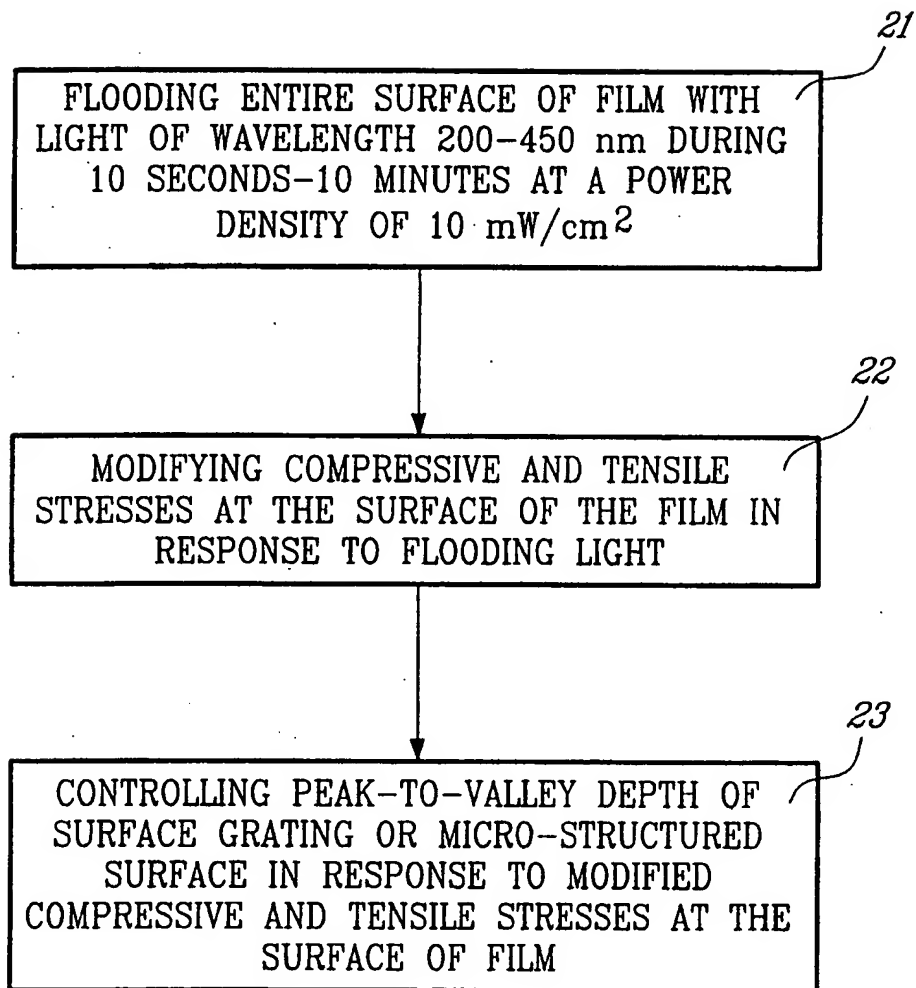


FIG. 1

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FIG. 2

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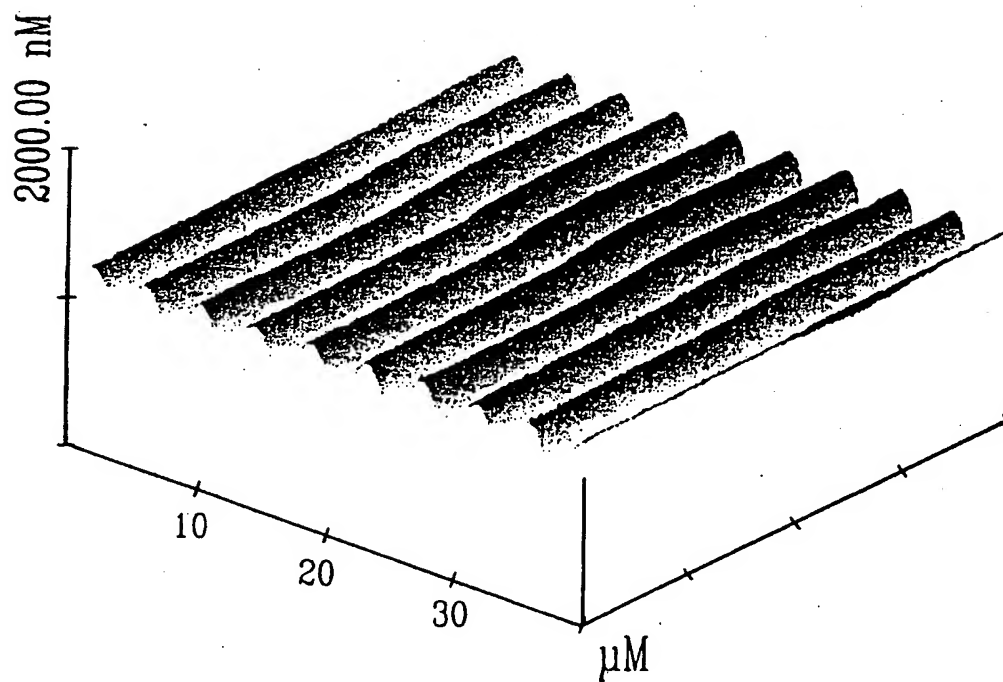


FIG. 3

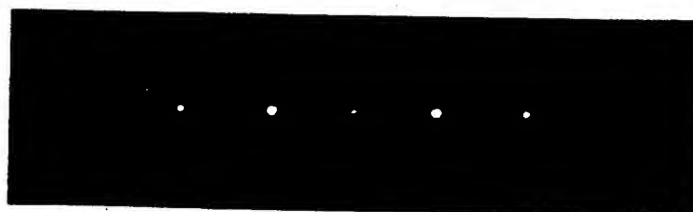
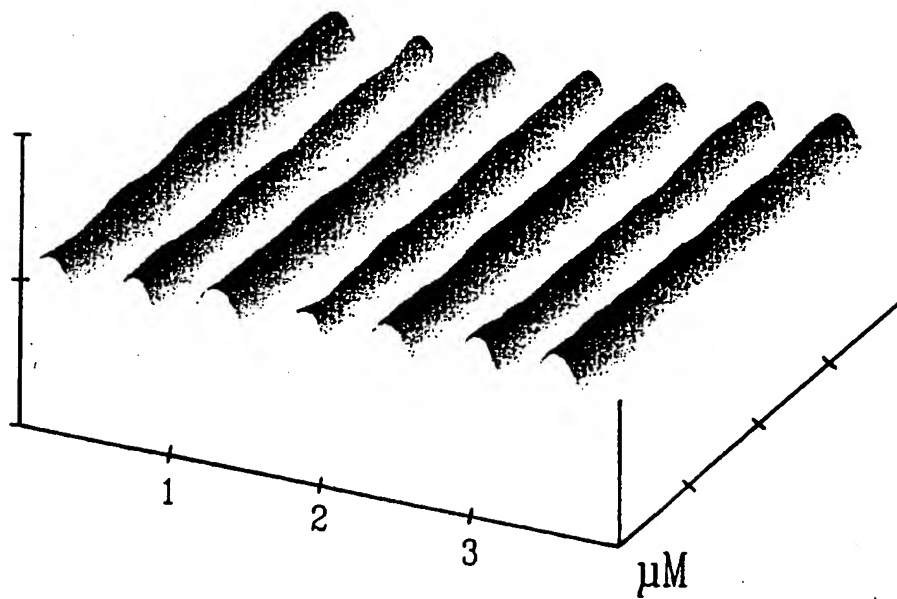


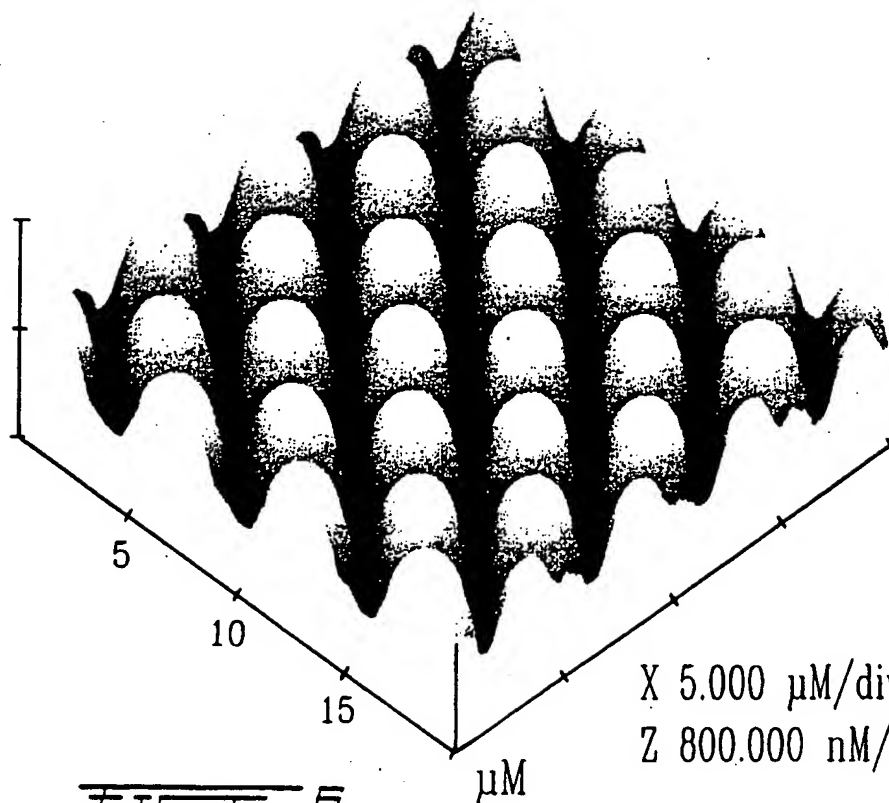
FIG. 4

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X 1.000 $\mu\text{M}/\text{div}$
Z 300.000 nM/div

FIG. 5



X 5.000 $\mu\text{M}/\text{div}$
Z 800.000 nM/div

FIG. 6

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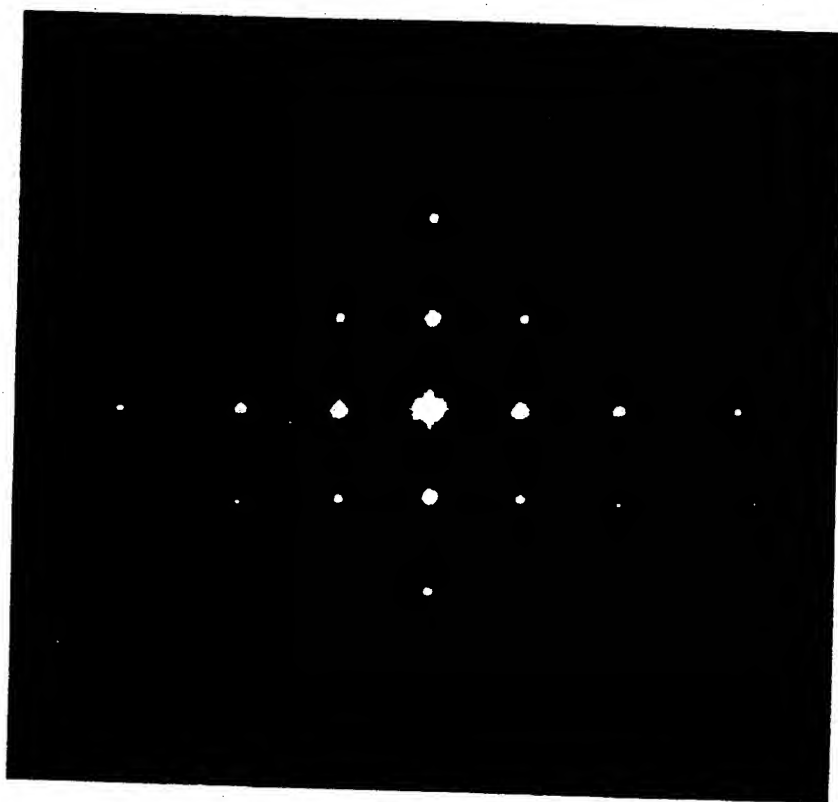


FIG. 7

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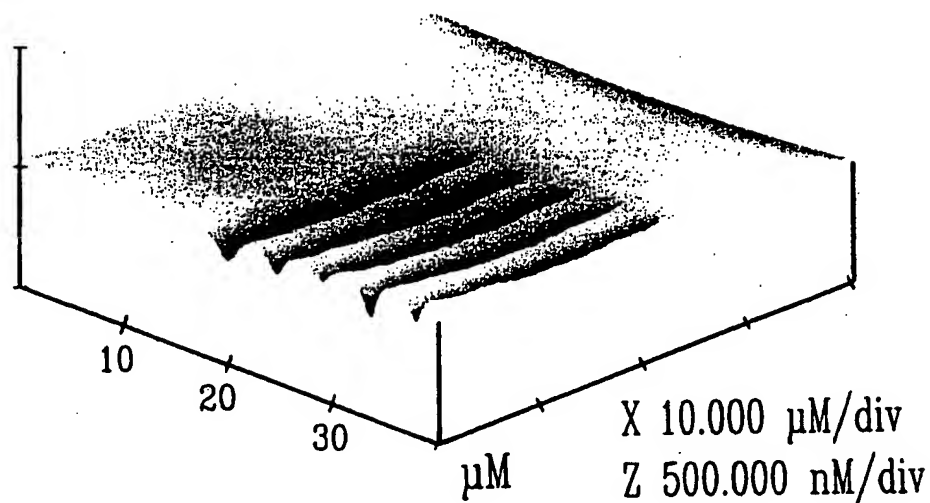


FIG. 8

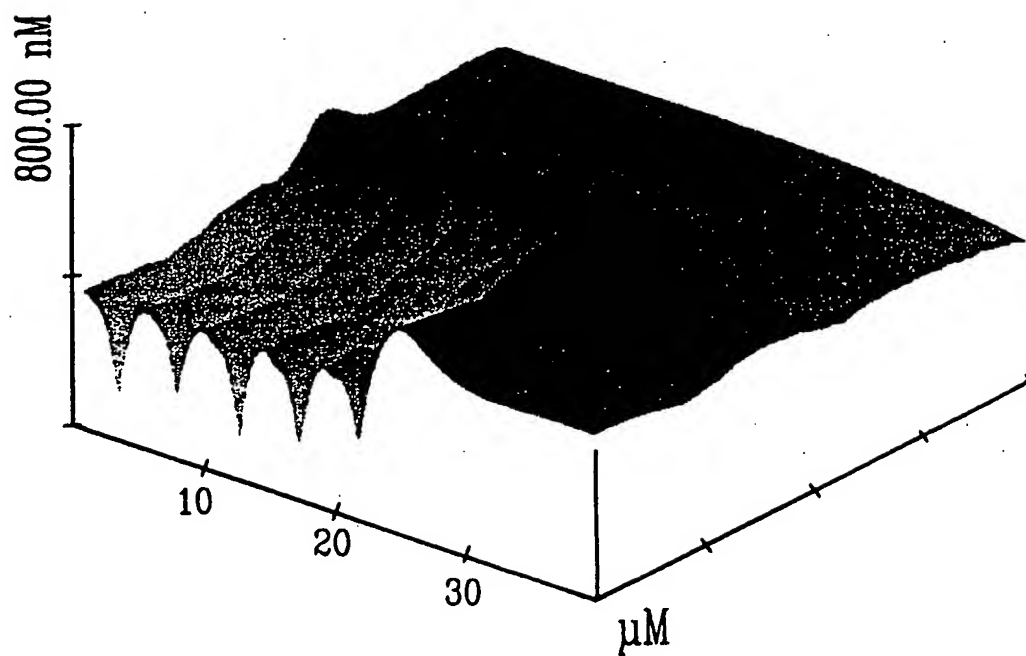


FIG. 9

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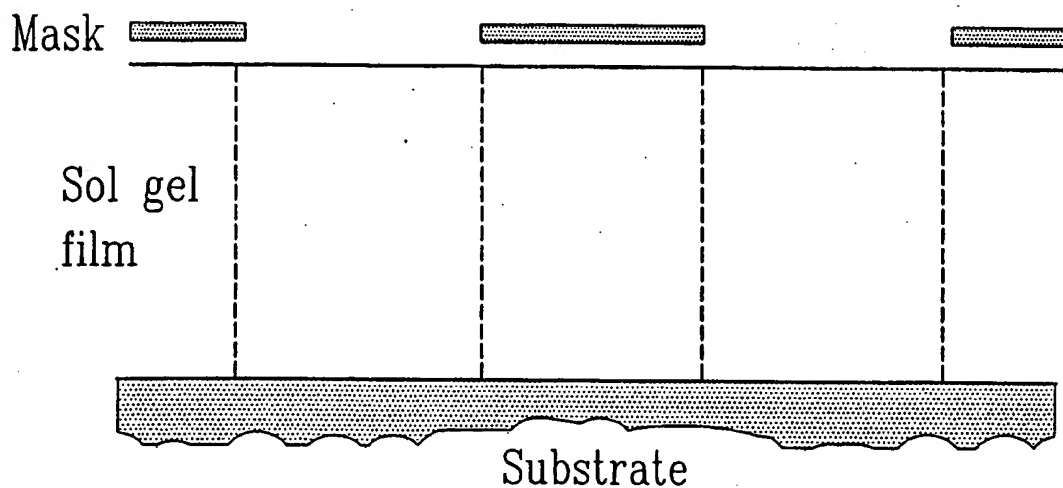


FIG. 10a

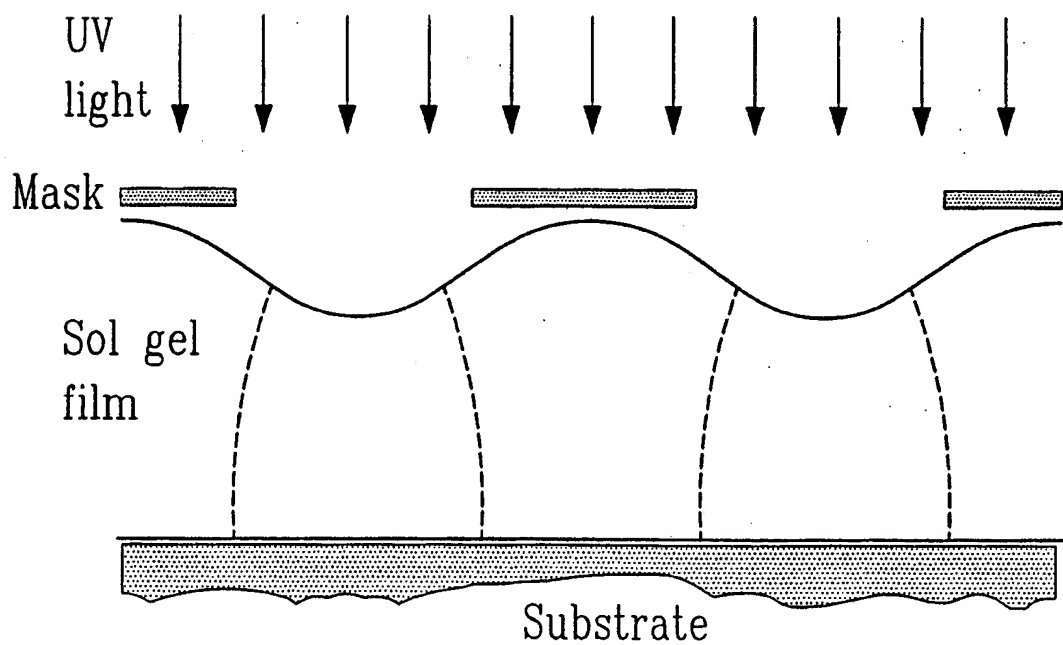


FIG. 10b

INTERNATIONAL SEARCH REPORT

International Application No

PCT/CA 00/01304

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 G03F7/00 G02B5/18 G03F7/004

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G03F G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, EPO-Internal, INSPEC, WPI Data, IBM-TDB, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>NISHII J ET AL: "PREPARATION OF BRAGG GRATINGS IN SPUTTER-DEPOSITED $\text{GeO}_2\text{-SiO}_2$ GLASSES BY EXCIMER-LASER IRRADIATION" OPTICS LETTERS, US, OPTICAL SOCIETY OF AMERICA, WASHINGTON, vol. 21, no. 17, 1 September 1996 (1996-09-01), pages 1360-1362, XP000627761 ISSN: 0146-9592</p> <p style="text-align: center;">--- -/--</p>	



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Date of the actual completion of the international search

19 March 2001

Date of mailing of the international search report

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Haenisch, U

INTERNATIONAL SEARCH REPORT

International Application No

PCT/CA 00/01304

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>SARAVANAMUTTU K ET AL: "Photoinduced structural relaxation and densification in sol-gel-derived nanocomposite thin films: implications for integrated optics device fabrication"</p> <p>CANADIAN JOURNAL OF CHEMISTRY, NOV. 1998, NATL. RES. COUNCIL CANADA, CANADA, vol. 76, no. 11, pages 1717-1729, XP002163177</p> <p>ISSN: 0008-4042</p>	
A	<p>EP 0 774 675 A (AGENCY IND SCIENCE TECHN)</p> <p>21 May 1997 (1997-05-21)</p>	
A	<p>PATENT ABSTRACTS OF JAPAN</p> <p>vol. 1998, no. 14,</p> <p>31 December 1998 (1998-12-31)</p> <p>& JP 10 253811 A (SANKYO SEIKI MFG CO LTD), 25 September 1998 (1998-09-25)</p> <p>abstract</p>	
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Int. l. Application No

PCT/CA 00/01304

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